Novel Composite Materials for SOFC Cathode-Interconnect Contact

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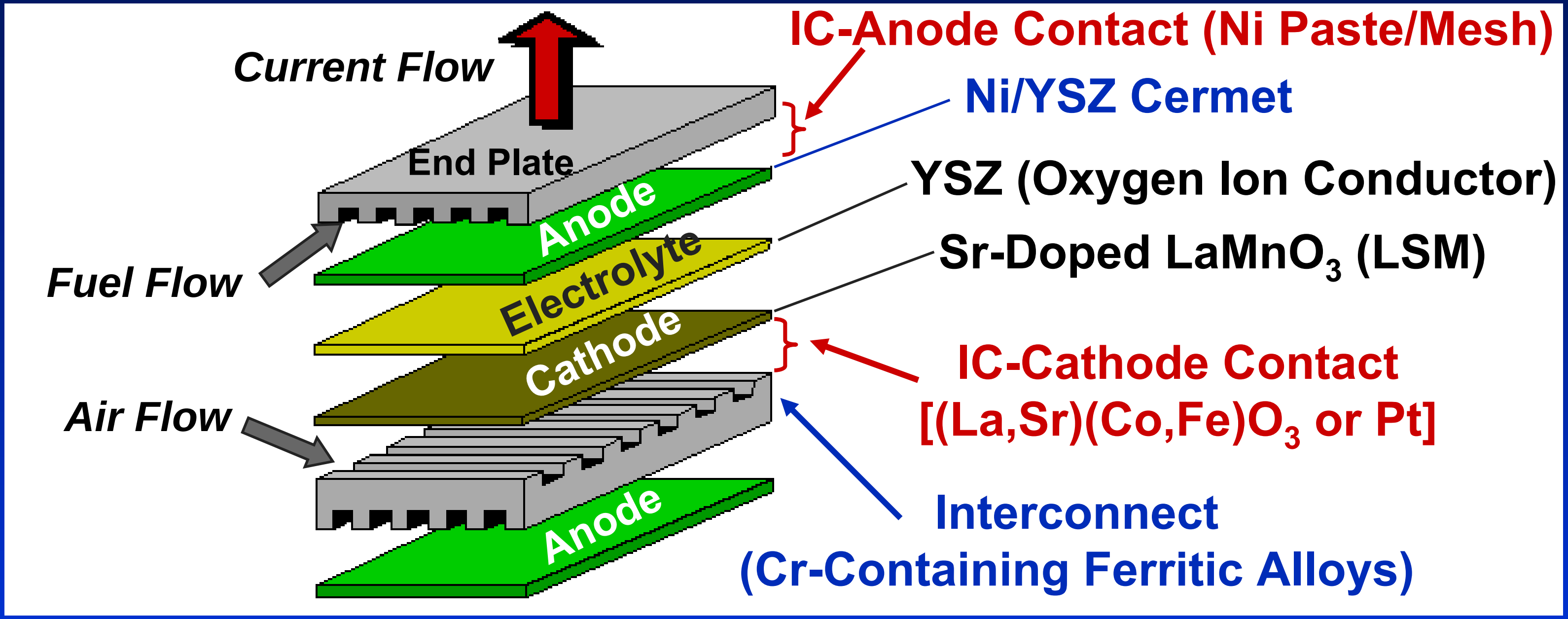
Grant Number: DE-FG26-05NT42533

Performance Period: Oct. 2007 – June. 2008

UCR Contractors Review Conference, Pittsburgh, PA, June 10-11, 2008

Electrical Contacts in SOFC stacks



- Electrical contact layers are used to reduce the electrode/ interconnect interfacial resistance by compensating for the corrugations present on their respective surfaces
- Ni-paste in combination with Ni-mesh is widely used to establish electrical contact between interconnect and Ni+YSZ anode.
- Finding a suitable material for electrical contact between the cathode and interconnect is challenging

Criteria for Cathode/Interconnect Contact Materials

- Sufficiently high electrical conductivity over SOFC lifetime
- Reasonable match in coefficient of thermal expansion (CTE) with other cell components
- Chemical stability under high current condition
- Stability with both the interconnect and cathode under oxidizing environment, especially negligible effects on the formation of protective oxides on interconnect alloy
- High sinterability at the SOFC operating temperatures
- Ability to buffer the interactions between interconnect oxide (usually Cr-containing) and electrode oxide
- Tolerance to thermal cycle-induced damage (possible self-healing if thermal cycle-induced cracking occurs in the contact layer)

Objectives of this Research Effort

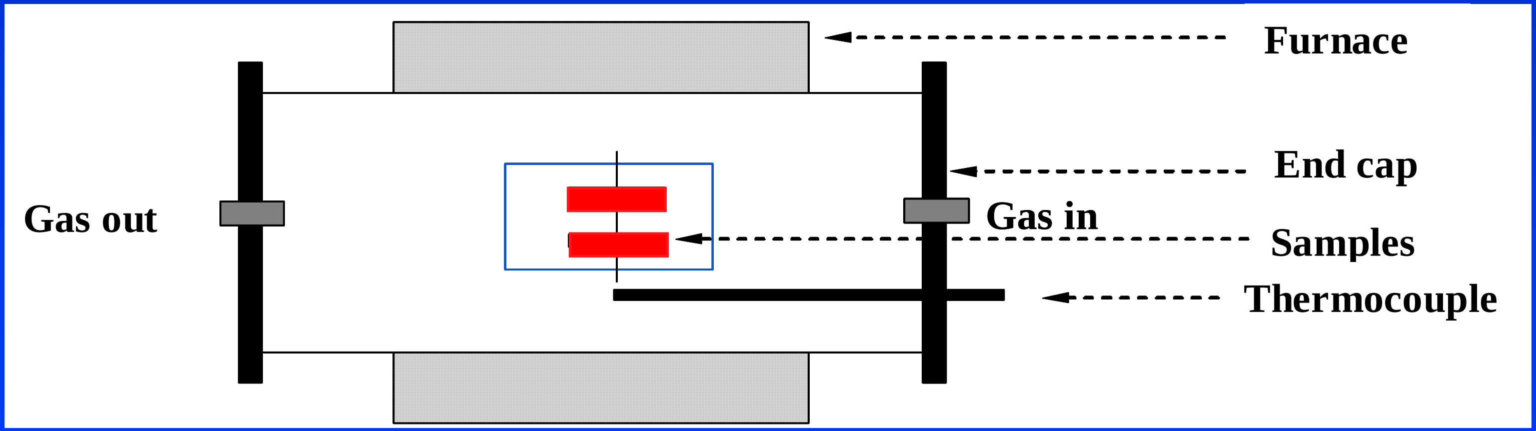
The overall goal of this project is to develop Ag-perovskite composites with reduced Ag evaporation, ability to absorb Cr from the interconnect, and adequate damage-tolerance as interconnect-cathode contact.

- **Elucidation of the mechanism of Ag evaporation at elevated temperatures**
- **Alloy design of new Ag alloys with reduced Ag evaporation/migration**
- **Optimization of processing and microstructures of the composite contact of Ag + perovskite [$(La_{0.6}Sr_{0.4})(Co_{0.8}Fe_{0.2})O_3$ – LSCF or $(La_{0.8}Sr_{0.2})MnO_3$ – LSM]**
- **Demonstration/assessment of performance of the new contact materials**

Ag Evaporation:
Pure Ag, Ag-base Alloys, and Composites

Ag Evaporation Testing

- Preparation of Ag evaporation samples
  - Ag-base alloys were prepared by arc melting, drop casting, followed by repeated cold rolling and annealing
  - Ag-perovskite composites were prepared by powder metallurgy
- The effect of various low-cost alloying elements such as Ti, Fe, Co, Ni, Mn, Sn, and Zn at levels of 1, 5, and 15at.% as well as noble metals such as Pd on the Ag evaporation rate were determined.
- The Ag evaporation behavior of the Ag+LSM and Ag+LSCF composites with different Ag-to-perovskite ratios was also evaluated.



Experimental Setup for Ag Evaporation Testing

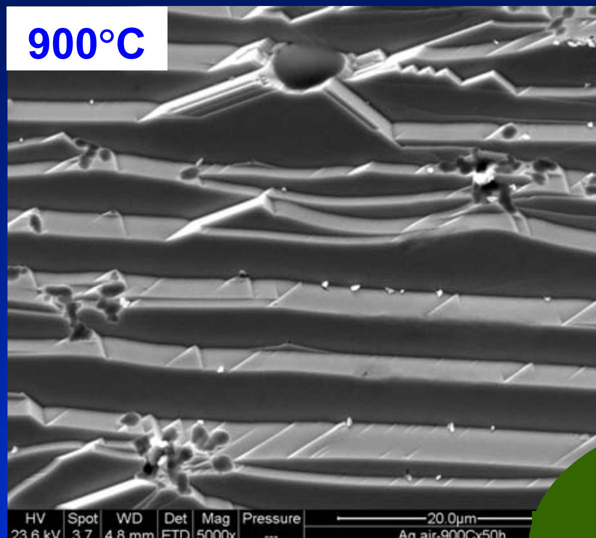
Effect of Atmosphere on Ag Evaporation

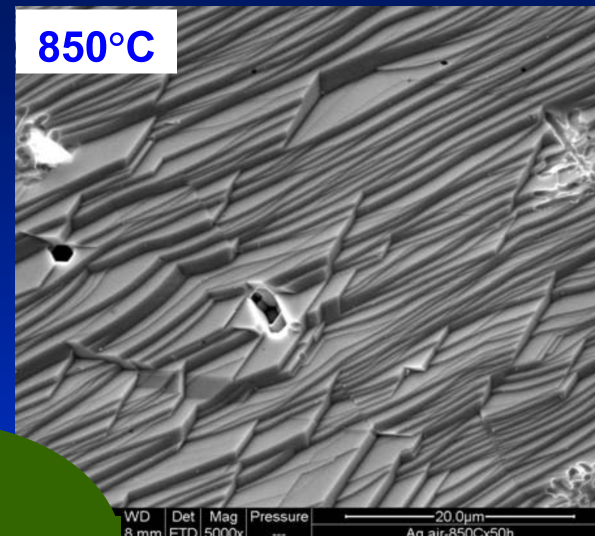
Atmosphere	Flow Rate ($cm.s^{-1}$)	Temperature (°C)	Evaporation Rate ($\times 10^{-9}$ $g.cm^{-2}.s^{-1}$)
$Ar+5\%H_2+3\%H_2O$	1.5	900	7.12
$Ar+5\%H_2$	1.5	900	7.06
$Air+3\%H_2O$	1.5	900	7.22
Air	1.5	900	7.11

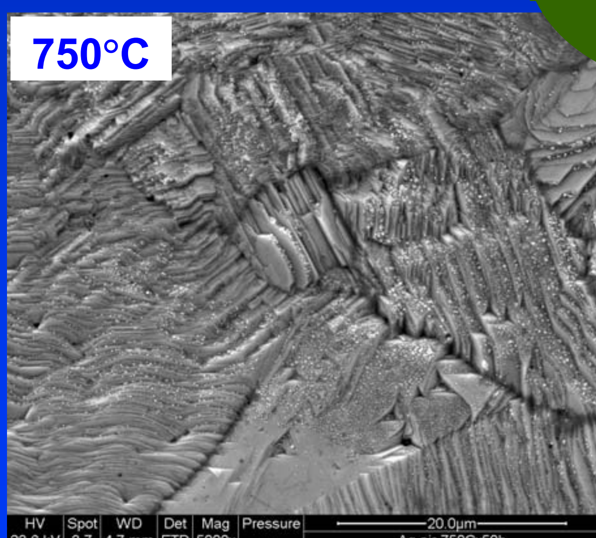
- The exposure atmospheres showed no measurable influence on the evaporation rate of Ag at 900°C.
- The essentially same evaporation rate in different environments indicates that the exposure atmosphere is not involved in the critical step that controls the Ag evaporation kinetics.
- The effect of atmosphere on Ag evaporation at lower temperatures are currently being evaluated.

Different surface morphologies were observed after evaporation test in oxidizing and reducing environments

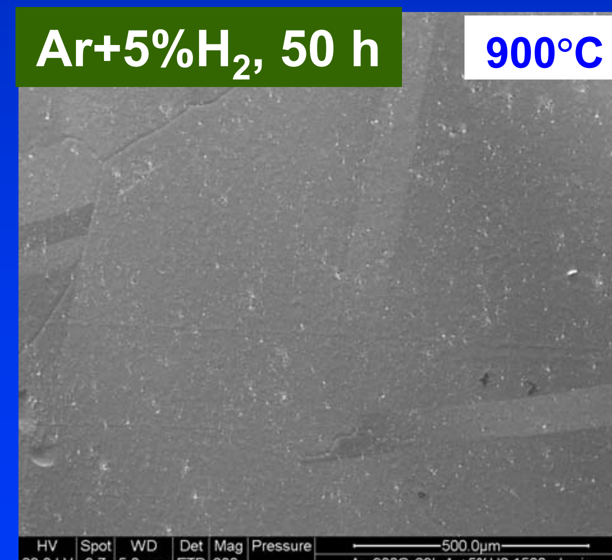
Air, 50 h







Ar+5%H_2, 50 h

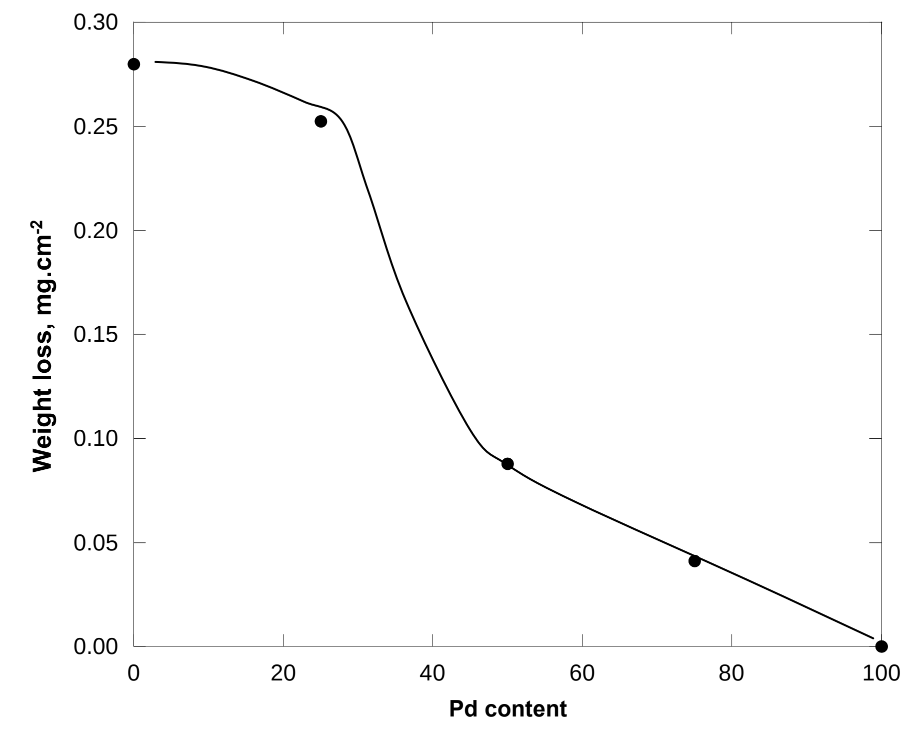


Plausibility of Ag as Cathode-Interconnect Contact

- At 800°C and air flow rate of 1.1 cm/s, the evaporation rate of pure Ag is 4×10^{-10} $g.cm^{-2}.s^{-1}$
- Considering the SOFC target lifetime of 40,000 h, this value is too high (0.06 $g.cm^{-2}$ or 60 µm)
- Since Ag evaporation is determined by the bonding of Ag atoms, alloy design should focus on identifying:
  - Alloying elements that drastically affect the bonding in Ag
  - Surface-active elements that block the surface Ag sites

Effect of Noble Metal Additions on Ag Evaporation

- With the addition of 25%Pt, Au, and Pd, some reduction in Ag evaporation rate in the range of 10-30% was observed for all the alloying elements.
- As the Pd content increased in the alloys, the Ag evaporation rate dropped consistently.
- Additions of the noble metals (Pt, Au, and Pd) were not practical due to high cost of the raw materials



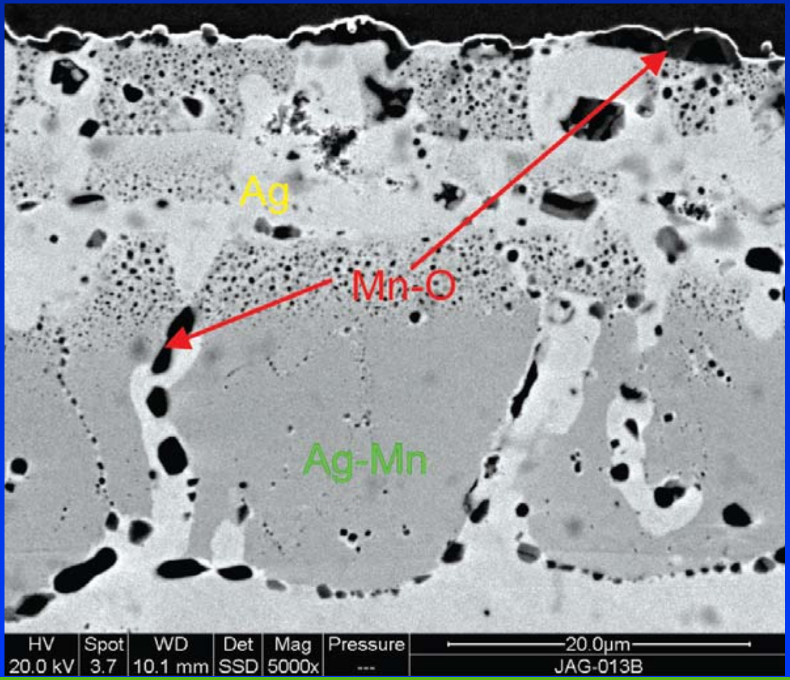
Weight losses of various Ag-Pd alloys after thermal exposure at 850°C for 40 hours in air with a flow rate of 1.5 $cm.s^{-1}$

Effect of Low-Cost Metal Addition on Ag Evaporation

- A significant reduction in weight loss was observed with the Mn and Zn additions into Ag after an initial exposure time; during subsequent exposures, however, a relatively constant evaporation rate similar to pure Ag was observed.
- This behavior was a result of selective oxidation of the alloying element, which led to the initial weight gain; furthermore, the thermally-grown oxide scale was highly porous, not effective in blocking Ag from evaporation.
- Alloying with small amounts of low-cost elements had no beneficial effect on the long-term Ag evaporation rate.

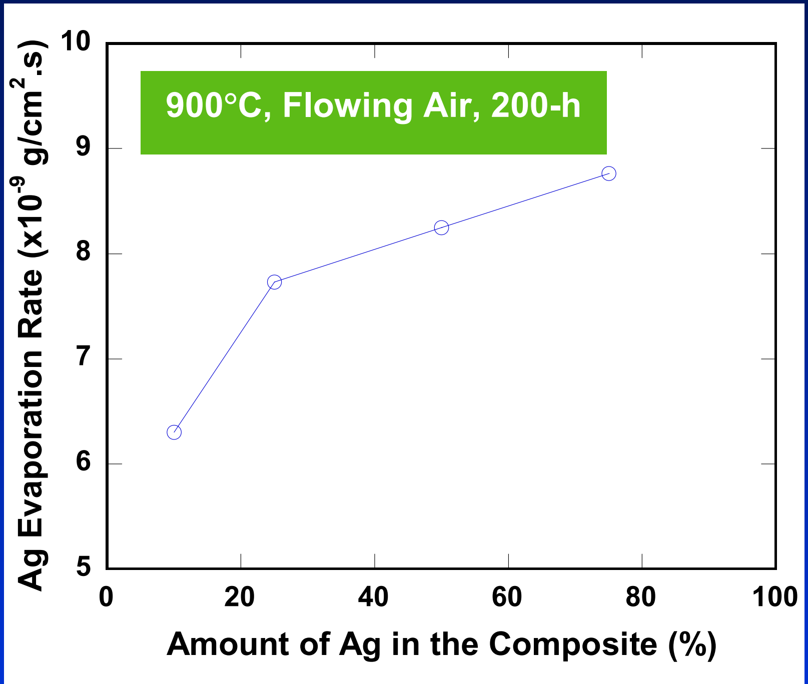
Ag Evaporation Rate at 800°C During 100-h Air Exposure for Ag-5%Mn

100-h Exposures	1st	2nd	3rd
Evap. Rate ($g/cm^2.s$)	$-6x10^{-9}$	$8x10^{-10}$	$7.5x10^{-10}$

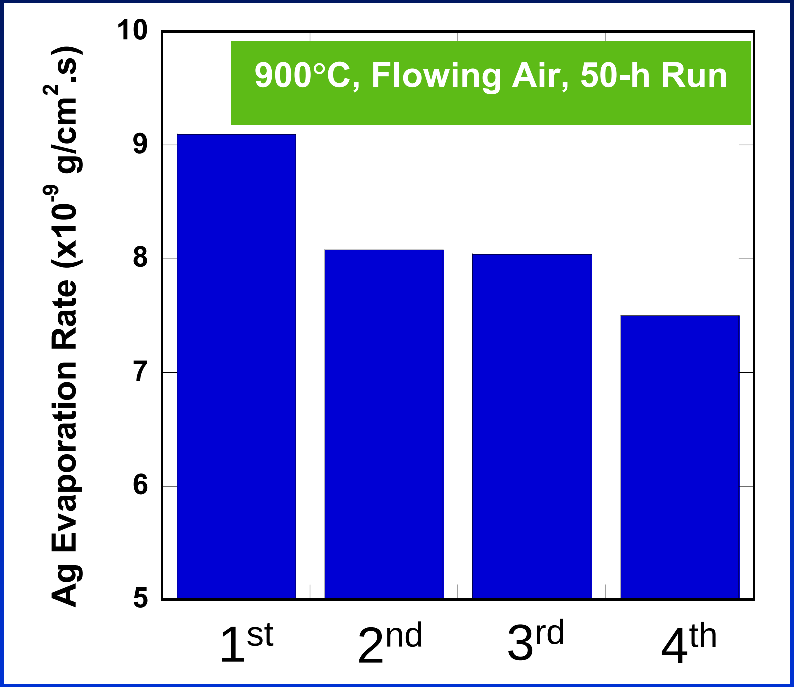


Cross Section of a Ag-15%Mn Coupon after 160-h Exposure to Air at 900°C

Ag Evaporation: Ag-Perovskite Composites



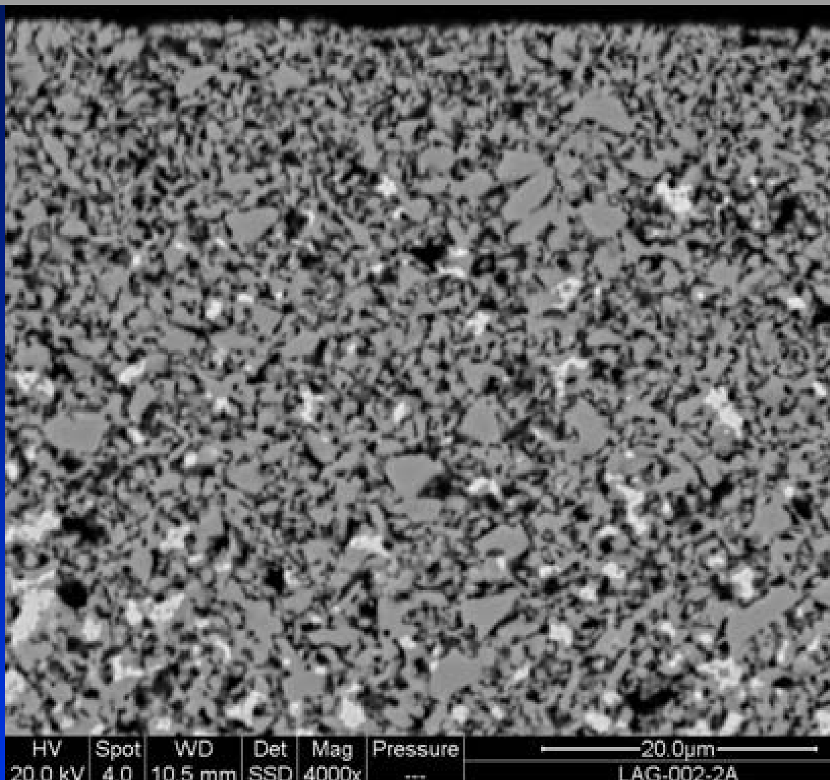
Effect of the Volume % of Ag in the Composite on the Evaporation Rate



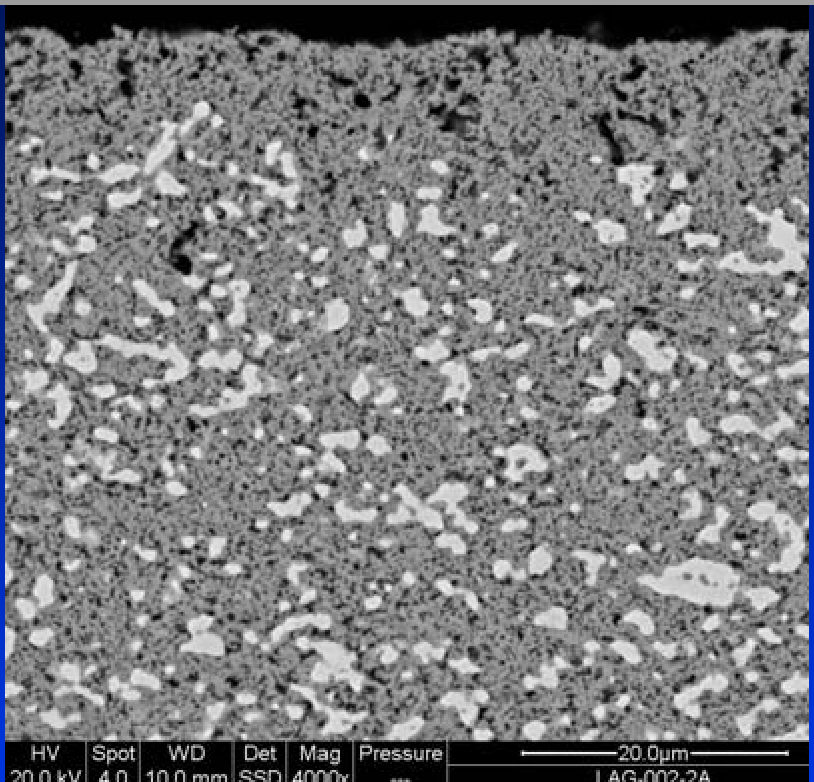
Ag Evaporation Rate of Ag-50%LSM as a Function of Exposure Time (Run)

- Composite materials of Ag+LSM exhibited a slightly reduced Ag evaporation rate as the amount of the perovskite phase increased. Even with 90%LSM, the evaporation rate was still pretty high, which can be attributed to the porous structure of the composite material.
- As the evaporation time increased, the Ag evaporation rate decreased slightly for the composite materials.

Ag Evaporation: Ag-Perovskite Composites



Cross-sectional View of Ag+LSM (25%Ag) after air exposure for 200 h



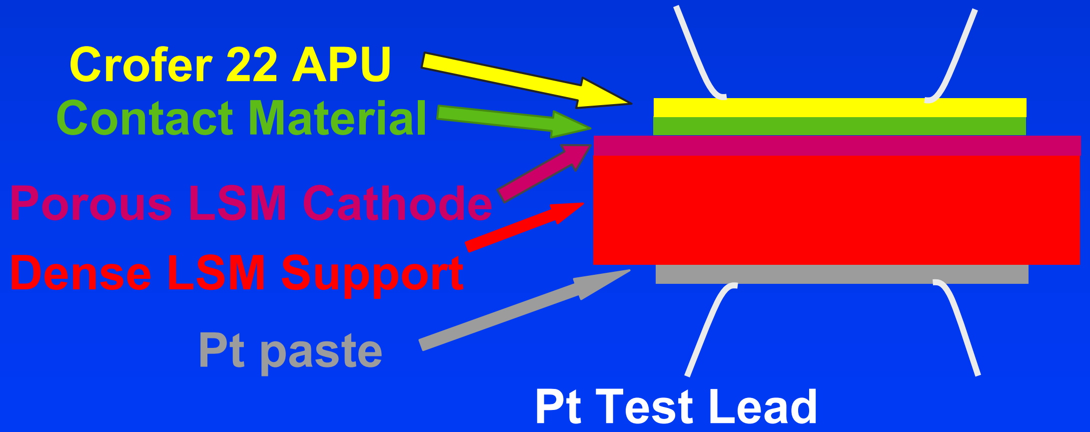
Cross-sectional View of Ag+LSCF (25%Ag) after air exposure for 100 h

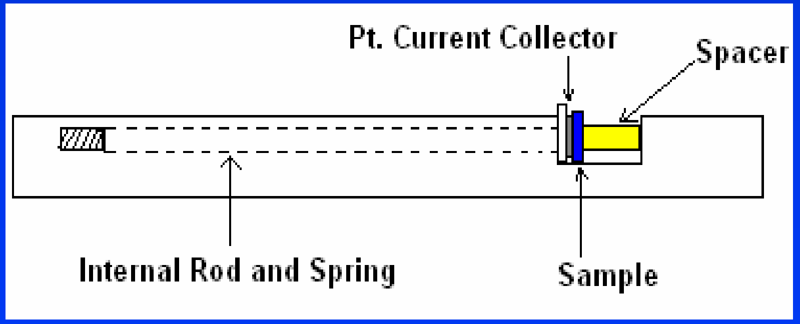
- A Ag-free zone near the surface was observed for both the Ag+LSM and Ag+LSCF composite, due to the porous structures.
- More extensive Ag depletion was observed for more porous structure and longer exposure.

Performance of Ag-Perovskite Composites as SOFC Contact Materials

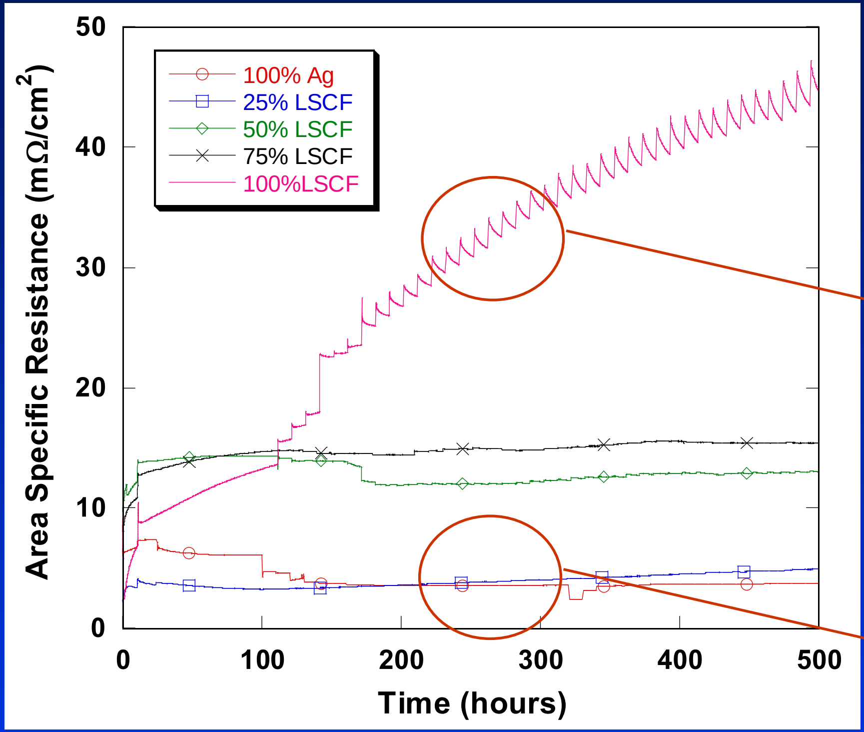
Evaluation of the Ag+Perovskite Composites

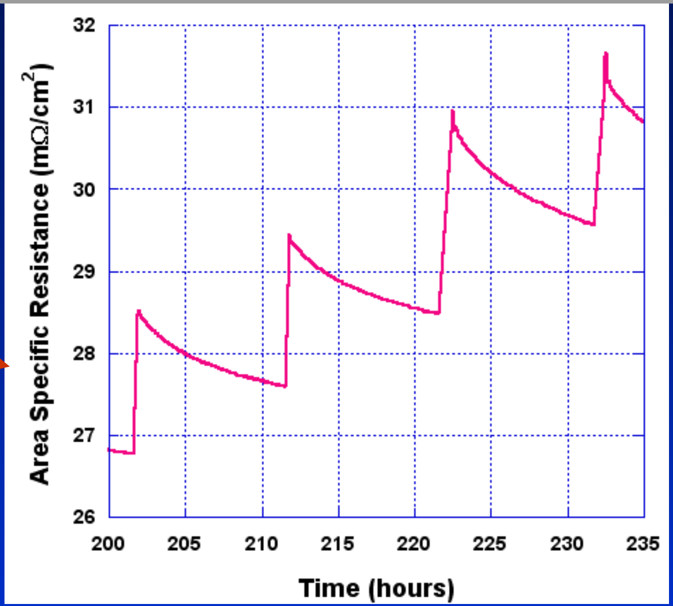
- A number of the Ag+LSM and Ag+LSCF composites with the Ag content of 0, 10, 25, 50, 75, and 100% (in volume) in the composite have been processed and interconnect/contact/cathode test cells with the Ag-perovskite composites as contact material have been constructed.
- The test cells were placed in the spring-loaded alumina rig to apply a small compressive load throughout testing, of ~0.16 kg/cm^2; a constant current density of 250 mA/cm^2 was used.
- The change in area-specific resistance (ASR) was recorded as a function of exposure time during isothermal or cyclic exposure.

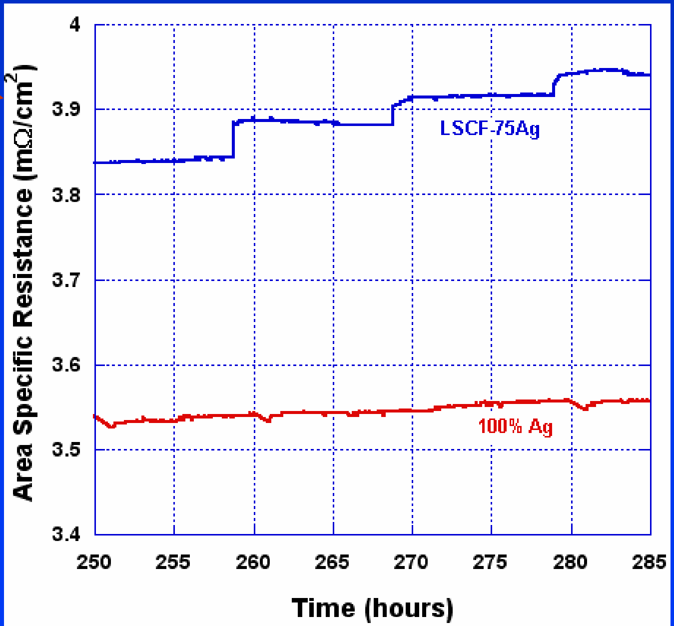




As Ag content increased in the Ag+LSCF composite, the ASR decreased correspondingly



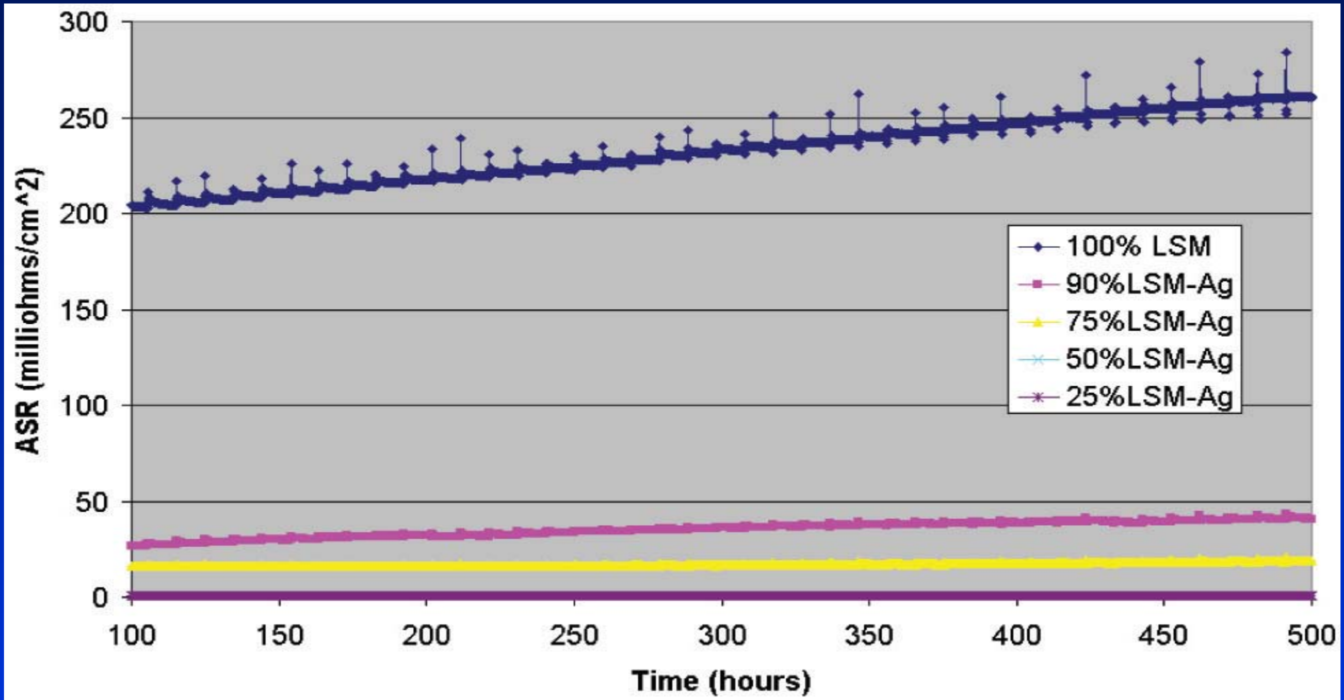




ASR change during thermal cycling (initial firing of 850ºCx10h; "break-in" of 800ºCx100h; 40 cycles with 800ºCx10h holding plus furnace cooling to 250ºC)

- Less damage was observed during thermal cycling for Ag-containing contact materials
- Some "self-healing" was observed for LSCF

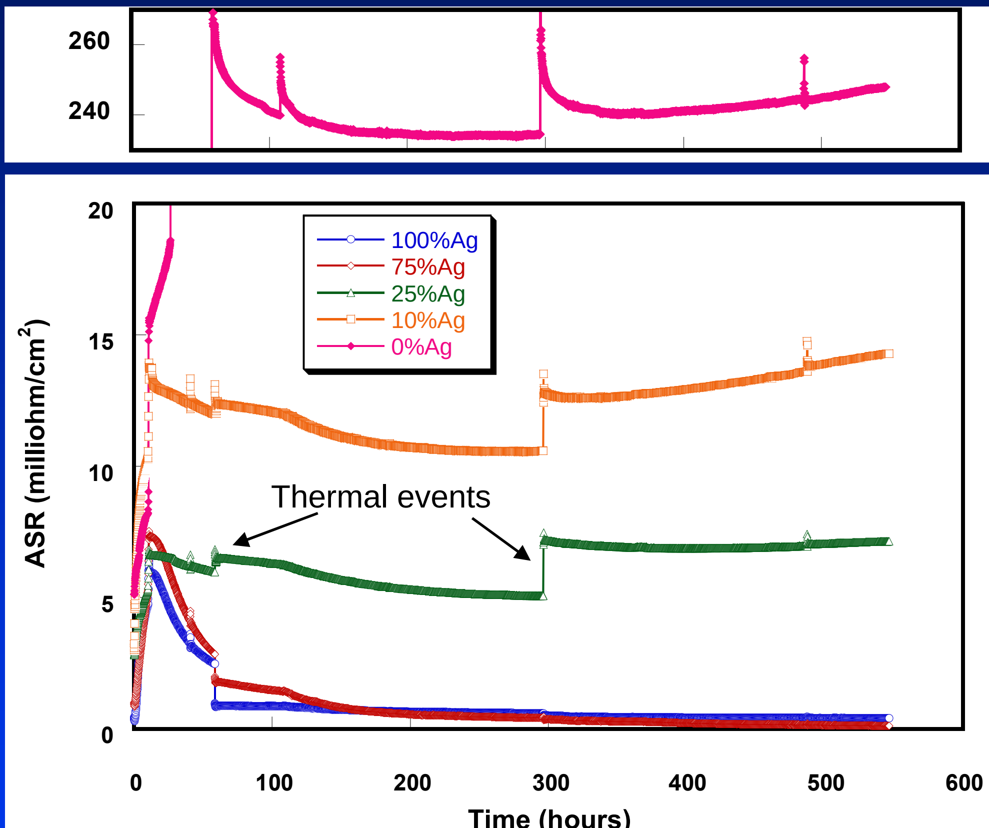
Similar results were obtained for the Ag+LSM composites during thermal cycling



ASR change during thermal cycling (50 cycles with 800ºCx10h holding plus furnace cooling to 250ºC)

- The pure LSM contact gave much higher ASR than pure LSCF; the addition of even 10% Ag into LSM drastically reduced the overall ASR
- Based on the projected values of the ASRs after 40,000 h using their rate of increase as determined from the figure, at least 25% Ag is needed to achieve the expected lifetime of 40,000 h and <100 mΩ/cm^2.

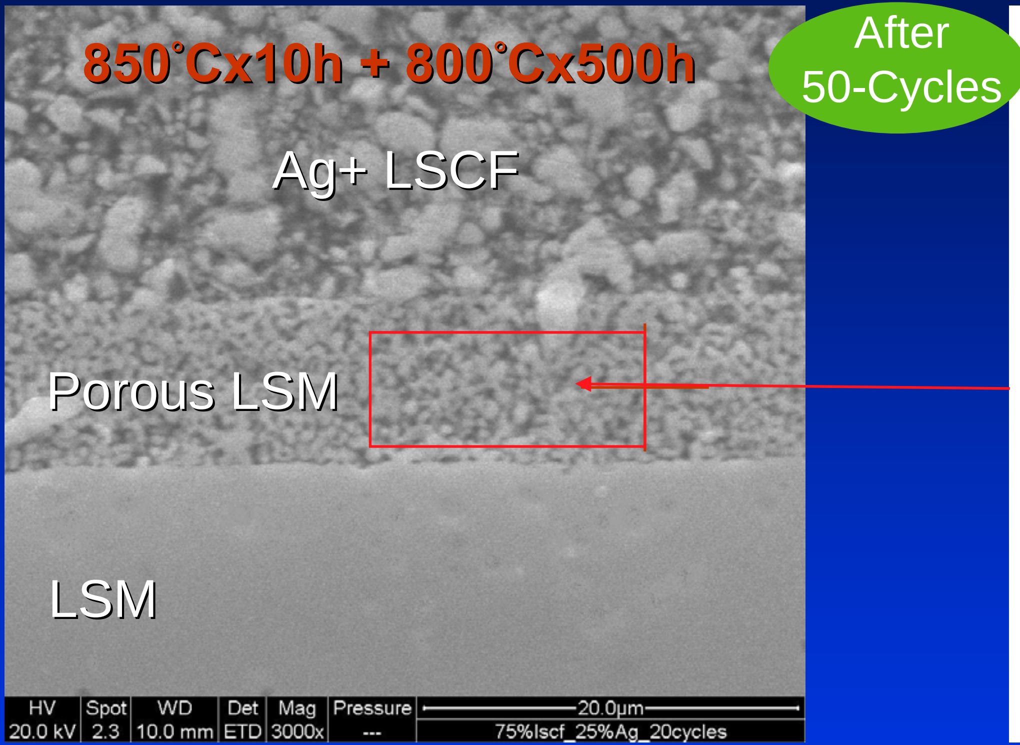
ASR Change of the Ag+LSM Composites during Isothermal Exposure



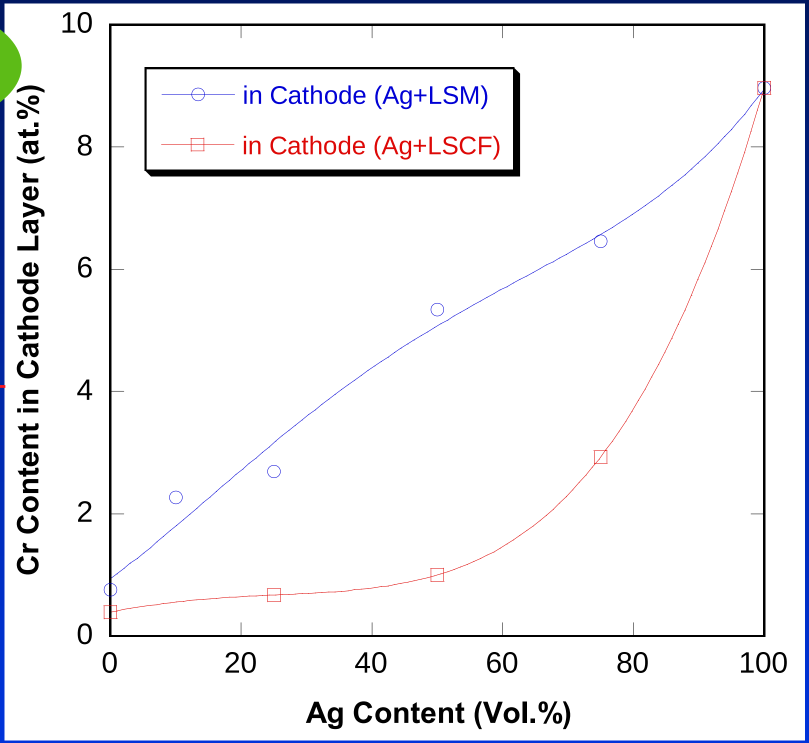
ASR Change during Isothermal Exposure with Occasional Cycling (Furnace Cooling to 250°C)

- **The pure LSM contact exhibited much higher ASR than other compositions; the addition of even 10% Ag into LSM drastically reduced the overall ASR**
- **The isothermally-exposed test cells exhibited ASR degradation rates that were an order of magnitude lower than the thermally-cycled test cells of the same composition.**
- **The feasibility of using composite contact pastes with less than 25% Ag addition was confirmed.**

With the increase of LSCF and LSM in the contact layer, Cr migration to the cathode was reduced



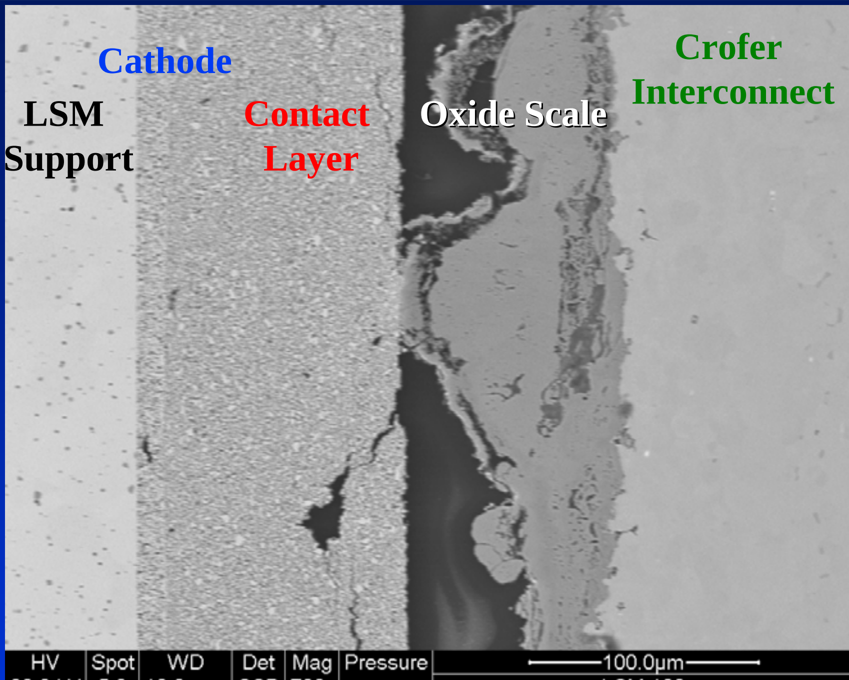
Cross-Sectional View of a Thermally-Cycled Cell



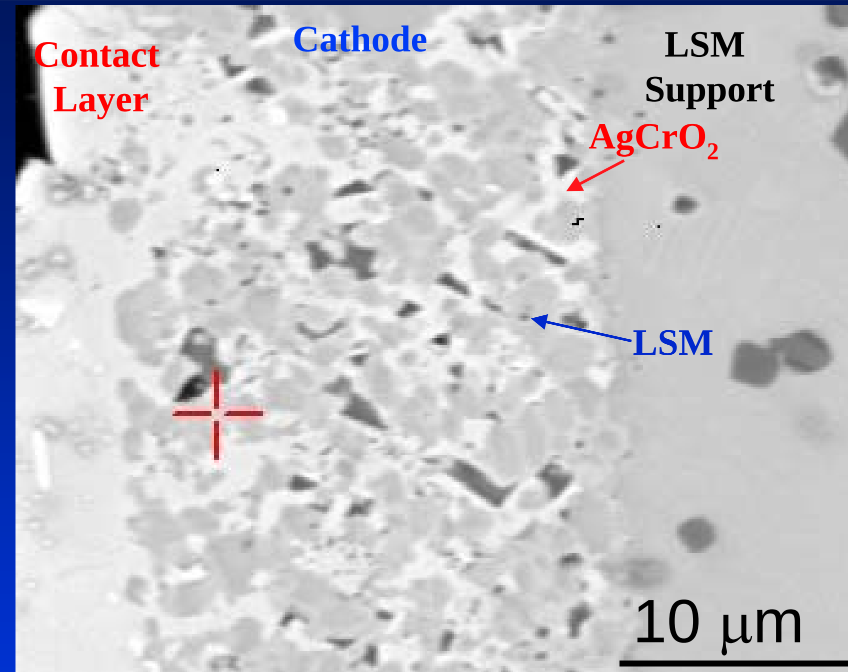
Cr Content in the Porous LSM Cathode

- A lower amount of Cr in the contact layer and a higher Cr content in the cathode was observed for the Ag+LSM contacts than for Ag+LSCF, implying LSM is not as effective as LSCF at trapping Cr within the contact layer.
- As the perovskite content in the contact increased, the Cr content in the porous LSM cathode decreased significantly.

SEM Cross-Sectional Observation of the Cycled Cells



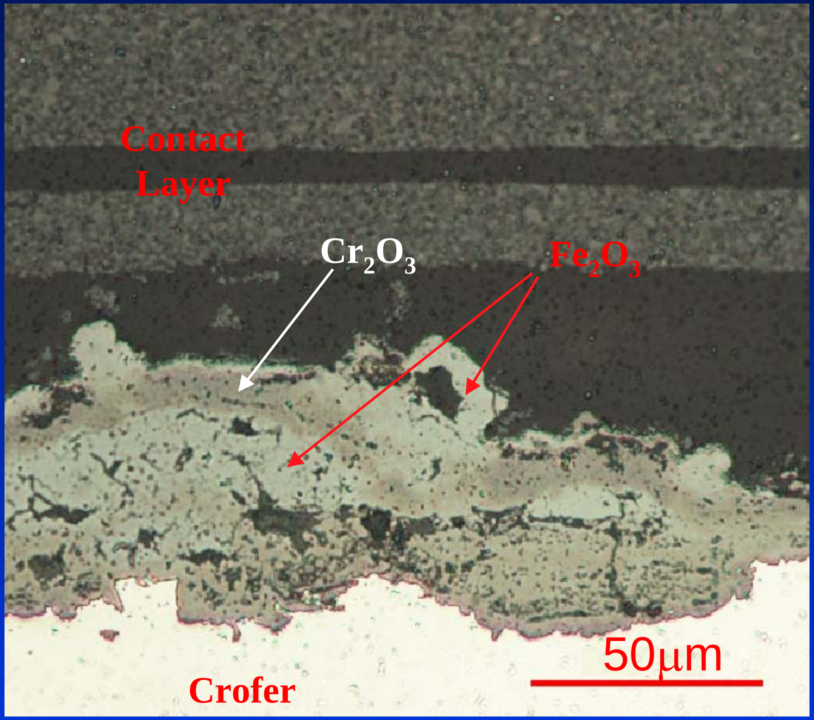
100% LSM Contact Material after Thermal Cycling



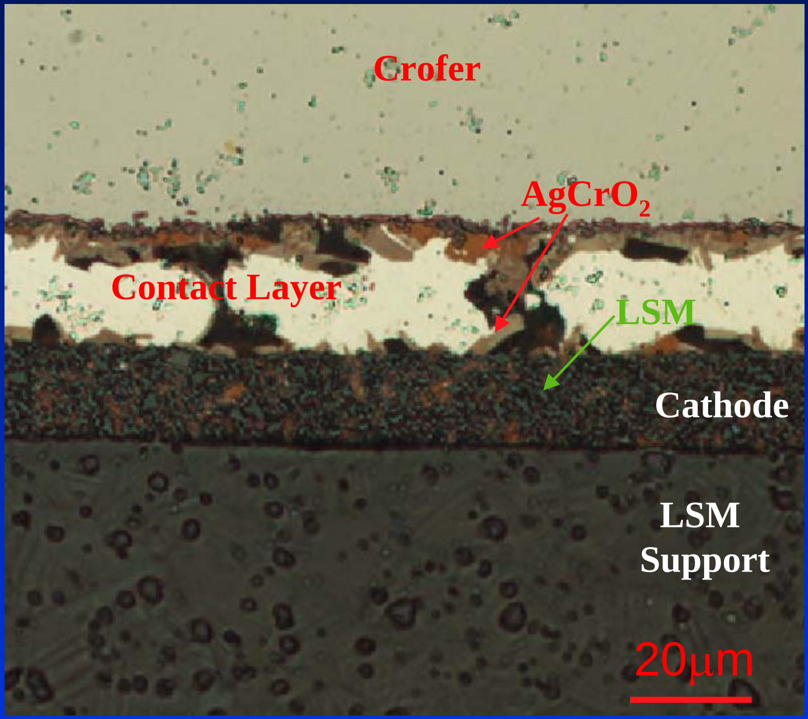
100% Ag Contact Material after Thermal Cycling

- The 100% LSM contact material proved to be very brittle in nature and separated from the interconnect upon removal from the test fixture.
- SEM analysis revealed the presence of a very thick layer of Fe_2O_3 on the interconnect for the 50-100% LSM contact material test cell
- Significant Ag migration into the cathode was observed for the Ag-containing contact materials, which led to the formation of $(Ag,Mn)CrO_2$.
- Similar results were observed for the cycled Ag+LSCF composites.

Similar results were observed for the Ag+LSM composites after isothermal exposure



100% LSM Contact Material after Isothermal Exposure



100% Ag Contact Material after Isothermal Exposure

- The presence of a very thick layer of Fe_2O_3 on the interconnect was confirmed for the 50-100% LSM contact cell after isothermal exposure with 2 cycles.
- Significant Ag migration into the cathode was observed for the Ag-containing contact materials, which led to the formation of $(Ag,Mn)CrO_2$.
- The interaction of Ag with the oxide scale thermally grown on the interconnect alloy also caused the formation of $(Ag,Mn)CrO_2$ at the interface.

Remaining Issues related to the Ag+Perovskite Composites

- Is the formation of the thick, non-protective oxide scale formed on the Crofer interconnect related to thermal cycling?
- What is the effect of current on the formation of such oxide scale?
- What is the effect of interconnect alloy composition and/or coating on the formation of such oxide scale?
- What is the minimum Ag content to achieve the adequate ASF during isothermal exposure?
- What is the role of Ag in reducing the ASR of the cell with the composite contact?
- Is there any more effective metal or oxide that can achieve similar results?

Acknowledgements

- This research was sponsored by Department of Energy (DOE) UCR Program under Grant # DE-FG26-05NT42533, Briggs White, Project Manager, DOE/NETL.
- Part of this work was also supported by the Center for Manufacturing Research, Tennessee Technological University.
- Contributions to experimental work from the following at TTU: John Batey, Brian Bates, and Wayne Hawkins.